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M ERCURY AS AN INDICATOR OF TEMPERATURE AND GEOCHEMICAL BARRIERS IN HYPERGENESIS ZONE OF GEOTHERMAL DEPOSITS (Kamchatka)

Rychagov S. N. [1], Nuzhdaev A. A. [1], Stepanov I. I. [2]

[1] Institute of Volcanology and Seismology of FED RAS, Petropavlovsk-Kamchatsky, 683006, Russia

E-mail: rychsn@kscnet.ru

[2] JSC "Alexandrovskaya Field Survey Company", E-mail: stepanovvi@mail.ru

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SYNOPSIS

The distribution of mercury in all the types of solid deposits presented in hypergenesis zone of the South Kamchatka geothermal fields is demonstrated: in rocks, in hydrothermally-altered rocks, in soils and soil-pyroclastic cover, in bottom sediments, in hydrothermal clays, in siliceous sinter deposits and in iron sulfides (Rychagov et al., 2009). Hg content ranges from background for the Kuril-Kamchatka region (1.0 – 1.5 x 10^{-6} %) in non-altered rocks to high and outstanding content (n x 10^{-2} %) in hydrothermal clays and monomineral pyrite samples. Data on sources, migration conditions and concentration mechanisms were acquired. Mercury is transported to the surface as a constituent of a deep-earth hydrothermal fluid and concentrates at the thermodynamic barriers in hydrothermal clays, in siliceous sinters (silica gel) and in soils with elevated salinity due to earth silicon, sulfates and other compounds precipitated from steam-water mixture. Newly-formed iron sulfides (pyrite), silicate gel and peat, found on surface of deposits and derived from plants that decayed under siliceous sinters, are good sorbents of mercury in geothermal conditions under atmospheric pressure and temperatures varying from 20^0C to 150^0C. Hg concentration levels in solid deposits and its distribution character in hypergenesis zone of geothermal deposits indicate thickness and probable depth of occurrence of a heat source.

1. INTRODUCTION

In recent years, attention to mercury behavior in the geological environment has significantly increased because of the wide distribution of this element in litho-, hydro- and atmosphere and in view of identification of new qualities in Hg migration, primarily, in geodynamically active regions of the world. Thus, the connection of anomalous variations of mercury content in water of active faults with present-day seismic activity of the Baikal Rift Zone is demonstrated (Koval et al., 2003). Lithochemical haloes of mercury dispersion in marine quaternary deposits localized along fluid-conducting faulting are used to detect and map sources of hydrocarbon resources (Astakhov et al., 2007). Study of mercury (Hg) behavior in geothermal deposits is traditionally associated with search tasks: identification and tracking of permeable zones, delineation of thermal anomalies, etc. (Trukhin et al., 1986). It is thought that under influence of an anomalously high convective heat flow practically all the mercury from host rocks is distilled off from depth and is accumulated in the thin near-surface layer of argillized rocks. We demonstrate that during the high temperature phase of hydrothermal-magmatic system development Hg may form anomalously high concentrations in fracture-breccia zones throughout the whole geological cross-section to a depth of 1.0 – 1.5 kilometer and while the system evolves the main body of mercury is gradually (?) transported to the surface (Rychagov, Stepanov, 1994). Mercury migration zones are localized in the central parts of systems and deposits and at the same time the connection of Hg flow with deep-earth (magmatic ?) sources is lost. Such a behavior of Hg in present-day geothermal conditions as well as the correlation of mercury distribution with Au, Ag, Pb, Cu, Zn and other elements in certain sections of the structure of hydrothermal-magmatic systems allows paying attention to Hg as to a possible indicator to formation mechanisms for temperature and geochemical barriers in hypergenesis zone of geothermal deposits.

2. RESULTS OF RESEARCHES

Sampling, sample preparation and analytical investigation were implemented using the standard technique (Rychagov, Stepanov, 1994) to case studies of the South Kamchatka best-known geothermal deposits – Mutnovsky, Pauzhetsky, Paratunsky and Nizhne(Lower)-Koshelevsky, and the thermal fields of the Kambalny volcanic ridge **(Figure 1)**. "Baseline" site was selected on the flank of Paratunsky geothermal deposit – a part of the geological structure where effects of anomalous heat flow are not observed. Initial bedding rocks, hydrothermally-altered rocks, argillites (hydrothermal clays), iron sulfides (pyrite) formed in hydrothermal clays, soil-pyroclastic deposits, siliceous sediments and travertines, salt exudates and bottom sediments were studied. All the objects are observed to have non-homogenous distribution of mercury depending on the type of solid deposits and confinedness to a certain geothermal deposit **(Table 1)**.

Study of mercury distribution in geological reference sections (wells) of the Okeansky geothermal deposit, located on the slope of active Baransky volcano (the Iturup island, the Greater Kuril Ridge), demonstrated that Hg created elevated concentration anomalies not only in near-surface zones but also at different depths (Rychagov, Stepanov, 1994). Rocks, on the whole, are enriched with mercury – an order higher than baseline values (Leonova, 1979) for the region. At the same time, Hg distribution is irregular from section to section. Relatively downthrownblocks, where rocks get cooled due to downward seepage of meteoric and mixed thermal waters, are observed to have alternating sections with low and high concentrations of Hg **(Figure 2*a*)**. Values of anomalously high mercury content correlate with zones of excessive fissuring and porosity of rocks, with decompaction zones at boundaries of lithological horizons and sulfidation zones. Accumulation of Hg is also observed in loose

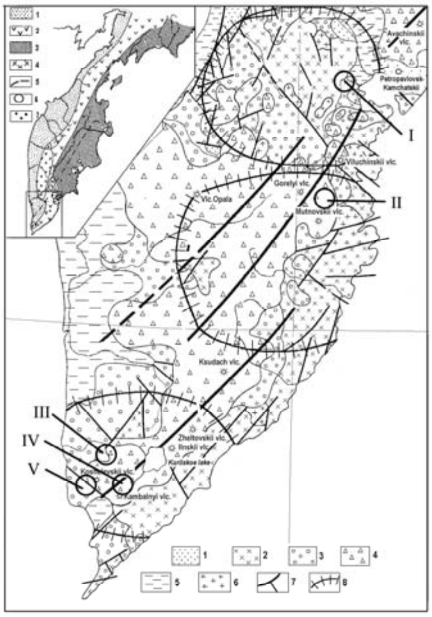

Figure 1. Geothermal Regions of South Kamchatka: the Structural Plan (Rychagov et al., 2006$_1$). Inset map: main structural areas of Kamchatka in Paleogene-Neogene time (made by G.M.Vlasov and V.V. Yarmolyuk in 1964): 1 – West-Kamchatka, 2 – Central Kamchatka, 3 – East-Kamchatka; 4 – Sredinny massif (Sredinny Ridge); 5 – boundary of the East-Kamchatka volcanic zone; 6 – geothermal regions; 7 – geothermal systems. Main map: 1 – Pre-Island-Arc-Stage rocks (Pre-Oligocene); 2 – Lower structural stage (Oligocene (?) – Middle Miocene); 3 – Middle stage (Middle Miocene– Pliocene); 4 – Upper stage – Quaternary volcanites; 5 – Quaternary and Pliocene - Quaternary (?) sedimentation masses of the upper structural stage of the internal area of the island arc; 6 – Large bodies of the quartz diorite complex; 7 – Faults; 8 – Boundary of geothermal areas, from North to South: Paratunsky, Mutnovsky-Zhirovsky and Pauzhetsky-Kabalny-Koshelevsky. Roman numbers indicate geothermal fields: I – Paratunsky, II – Mutnovsky, III – Pauzhetsky, V – Lower-Koshelevsky; and thermal manifestations of Kambalny Ridge (IV).

clastic rocks emplaced between lava flows and andesite sills. Lava flows and subhorizontally bedded sills and dykes noted for low permeability for steam-hydrothermae and gases, apparently, act as screens for a fluid saturated with mercury vapor. On the other hand, mercury concentrations in liquid-vapor transition zones are usually not higher than baseline values. Probably, in the conditions of boiling zone thermodynamic barriers, mercury easily migrates across the section. Sections are virtually barren in the upstanding blocks of rocks **(Figure 2*b*)**, - only minute Hg concentration anomalies are registered. High temperature of rocks in such blocks (up to 380-470^{0}C at a depth of 800-1000 meters), governing fluxes of an ascending high-temperature fluid causes migration of mercury from fracture-interstitial space and minerals' crystal lattice towards the day surface. Thus, within the structure of the Baransky hydrothermal-magmatic system being at the progressive development stage, mercury is an indicator of higher permeability zones, temperature conditions and, apparently, ore geochemical barriers, including the ones at a depth of over 500-1,000 meters.

Table 1. Average values of concentration of mercury in various types of sediments on geothermal deposits of Southern Kamchatka

Type of sediments	Hg, 10^{-7} %			
	Geothermal deposits			
	Pauzhetsky	Nizhne-Koshelevsky	Mutnovsky	Paratunsky
Rocks	**16** / 220	**16** / 220	**136** / 13	**29** / 42
Metasomatites	**75** / 220	**75** / 220	**1184** / 5	**217** / 22
Soils	**523** / 50	**2010** / 62	**510** / 38	**106** / 34
Bottom sediments	**102** / 42	-	**977** / 56	-
Siliceous deposits	**19** / 34	-	-	-
Hydrothermal clays	**2727** / 250	**15350** / 48	**5000** / 32	-
Pyrite	**7280** / 57	-	-	-

The note. Definitions are executed in Institute of Volcanology and Seismology FED RAS by atom-fluorescent method. Analysts I.I. Stepanov, N.I. Chebrova, N.I. Svinuhova and V.P. Korosteleva. In numerator – average values of concentration of mercury in tests, in a denominator – quantity of definitions.

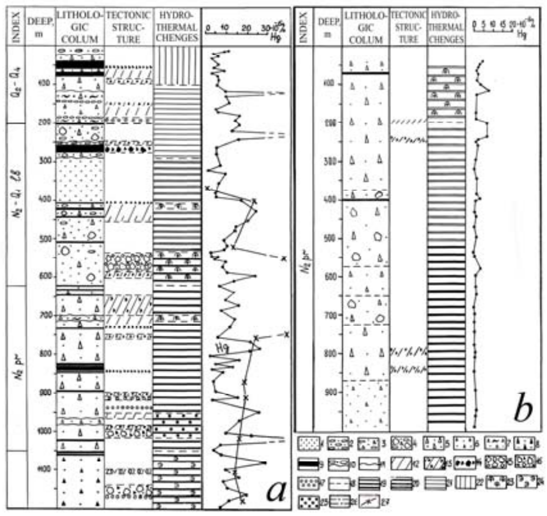

Figure 2. Geological cross-sections of Baransky system (Rychagov, Stepanov, 1994), *a* – downthrown block (well 54), *b* – upstanding block (well 65). 1 – tuffites; 2 – gravel; 3 – tuff gravel; 4 – tuff conglomerates; 5 – psephitic tuffs of andesite-dacitic composition; 6 – same psammitic; 7 – ignimbrites and pumice tuffs; 8 – intrusive breccias; 9 – effisives, dykes and sills of andesite-basalt composition; 10 – diluvium; 11 – stratigraphical boundaries; 12 – fissure zones; 13 – tectonic breccias; 14 – near-contact breccias; 15 – hydrothermal breccias; 16 – polymictic combined breccias; 17 – areas of higher porosity rocks; 18 – boundaries of tectonic zones and metasomatites facies; 19 – mid-temperature, 20 – low-mid-temperature, 21 – low-temperature propylites; 22 – rocks of sulfuric leaching zones; 23 – hydrothermalites of boiling zones; 24 – elevated content of epidote; 25 – same of sulfides; 26 – boundaries of geochemical anomalies; 27 – content of mercury in pyrite monofractions.

The study of mercury distribution in hypergenesis zone of the South Kamchatka geothermal deposits demonstrated that behavior of this chemical element is ambiguous and depends on temperature and physical-chemical conditions of formation and alteration of various geological sediments. Rocks occurring on the day surface, at large, contain low and baseline for Kuril-Kamchatka region (Leonova, 1979) values of Hg concentrations. However, Mutnovsky geothermal deposit is notable for high average Hg concentration values in non-altered rocks of various origin (lavas, tuffs, ignimbrites, breccias), and in other solid sediments too – metasomatites, soils, clays and others **(Figure 3)**. In our opinion, it is primarily due to difference of the Mutnovsky deposit and Mutnovsky hydrothermal-magmatic system from the other studied sites by a number of general parameters: higher installed and forecast capacity (62 and over 300 MW_e, respectively), long-lasting (during the whole quaternary period) hydrothermal-metasomatic changes of huge rock mass ($\geq$ n x 100 km^3), wide exposure of argillizite sequence on the surface ($\geq$ n x 10 km^2), presence of a large long-lived heat and ore feed source in the interior of the hydrothermal-magmatic system. Hydrothermally altered rocks as well as considerable soil-pyroclastic deposits all the way through the hypergenesis zone contain mercury concentrations by 1-2 orders higher than the baseline values. The same is characteristic of bottom sediments studied in detail at two geothermal deposits – Pauzhetsky and Mutnovsky. Accumulation of mercury in the indicated formations is associated with present-day hydrothermal process and presence of rock-forming and secondary mercury-concentrating minerals in metasomatites, soils and bottom sediments. To some extent, studies of hydrothermal clay strata and artificial siliceous sinter deposits may explain conditions and mechanisms of mercury accumulation and redistribution in various parameters of geothermal environment.

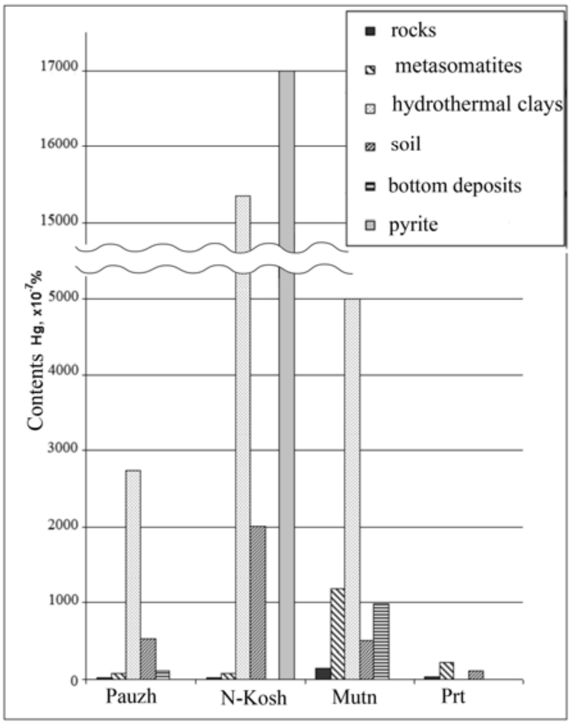

Figure 3. Content of Hg in various types of solid deposits at Pauzhetsky (Pauzh), Nizhne(lower)-Koshelevsky (N-Kosh), Mutnovsky (Mutn) and Paratunsky (Prt) geothermal fields.

It had been demonstrated earlier that a high level of mercury content in hydrothermal clays is mainly caused by its accumulation in clay minerals at the temperature barrier (Stepanov et al., 1982). At the same time, pyrite is a proficient concentrator of mercury in hydrothermal zones. This point is confirmed by studies of hydrothermal clay sections of Nizhne(Lower)-Koshelevsky thermal anomaly and Verkhne(Upper)-Pauzhetsky geothermal field. The latter has high Hg concentrations associated with near-surface horizon of blue clay (up to $\geq 2 \times 10^{-4}$ %), where quantity of pyrite may amount to 90 % of volume. At the same time, monomineral pyrite samples yield Hg concentrations by 1-2 orders higher. Hydrothermal clays in the sections of the Nizhne(Lower)-Koshelevsky thermal anomaly are characterized by generally higher content and by relatively even distribution of pyrite in layers (up to 30-40 volume %); concentrations of Hg in bulk clay samples amount to n x 10^{-3} %, in pyrite monofractions – n x 10^{-2} %. Thus, pyrite is a good concentrator of mercury, as well as gold, polymetals and other elements, which was demonstrated not only for epithermal ore deposits but also for the present-day geothermal conditions (Structura…,1993).

Siliceous sinter deposits of the Pauzhetsky geothermal field contain mercury, on the average, within (1-3) x 10^{-6} %, which corresponds to baseline values for solid deposits under the conditions of hydrothermal process. Siliceous sinters deposited by a thermal spring may be noted for high Hg concentrations (by one order higher than the baseline values). There is also a trend for mercury concentrations to decrease from the upper layer of deposits to the lower one and from the beginning of "coat" formation down along the strike. The represented data are indicative of the fact that input of mercury occurs from deep-earth hydrothermal flux (the exploited water-bearing horizon in this section of Pauzhetsky deposit is averagely located within a depth range of 600-800 m) and it is concentrated together with colloid silica acid at the first thermodynamic barrier – at well top. Probably, silica gel, along with vegetation substrate is good mercury sorbent. When silica gel ages and silicon minerals form, mercury residing here in the atomic form can easily escape from the lattice or from defective mineral structure and migrate towards the foundation of the section and along with the flux.

A high level of Hg concentration in soils in the central parts of the geothermal deposits is caused by the following reasons: 1) intensive emanation of mercury from the host rocks (deep-earth source?) under the impact of anomalously high temperatures of an ascending heat flow, detected for the Nizhne(Lower)-Koshelevsky and Mutnovsky deposits, and its accumulation in near-surface rocks at the temperature barrier; 2) formation of thermodynamic and geochemical barrier in the foundation of soil profile, namely, due to precipitation of a number of salts (sulfates, cryptocrystalline silicon earth from silica gel, etc.), which can be mercury sorbents. Peat buried under modern siliceous sinters deposited by thermal waters of Pauzhetsky deposit (**Figure 4**) can be also considered a good Hg sorbent. Sorption properties of the peat bed are probably influenced by high openness of system "siliceous sinter – vegetative substrate" as a result of active and ongoing circulation of thermal waters, and by intensive processing of buried vegetation in an elevated temperature environment.

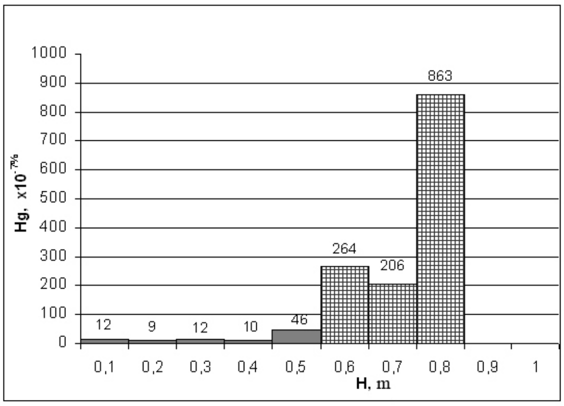

Figure 4. Distribution of mercury concentrations by layers of vertical section of mass of siliceous sinter deposits in the point 30 meters away from top of well R-120. Three lower layers are composed of peat formed during 25-27 years due to conservation and transformation of plant remains under the layer of siliceous deposits under the conditions of constant elevated temperatures (75-90^{0}C); intermediary layer (0.5 – 0.6 m) is composed of thin mud precipitation.

3. CONCLUSION

To sum up, we have received new data on sources, migration conditions and mechanisms of mercury concentration under the conditions of geothermal systems. Based on continued studies, the distribution of mercury in all the types of solid precipitations manifested in hypergenesis zone of the South Kamchatka geothermal deposits is demonstrated: in rocks, in hydrothermally-altered rocks, in soils and soil-pyroclastic cover, in bottom sediments, in hydrothermal clays, in siliceous sediments and in iron sulfides (Rychagov et al., 2009). Hg content ranges from background for the Kuril-Kamchatka region (1.0 – 1.5 x 10^{-6} %) in non-altered rocks to high and outstanding grades (n x 10^{-2} %) in hydrothermal clays and monomineral pyrite samples. Data on sources, migration conditions and concentration mechanisms were acquired. Mercury is transported to the surface as a constituent of a deep-earth hydrothermal fluid and concentrates in thermodynamic barriers in hydrothermal clays, in siliceous sediments (silica gel), in travertines (calcic gel) and in soils with elevated salinity due to earth silicon, sulfates and other compounds precipitated from steam-water mixture. Newly-formed iron sulfides (pyrite), silicate gel and peat, found on surface of deposits and derived from plants that decayed under siliceous sinters, are good sorbents of mercury in geothermal conditions under atmospheric pressure and temperatures varying from 20^{0}C to 150^{0}C. Hg concentration levels in solid precipitations and its distribution character in hypergenesis zone of geothermal deposits indicate thickness and probable occurrence depth of the heat source.

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